PATENT SPECIFICATION

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805,111

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COMPLETE SPECIFICATION

Hydroforming of Naphthas

We, ESSO RESEARCH AND ENGINEERING COMPANY, a corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Elizabeth, New Jersey, United States of America, do hereby declare this invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to an improved hydrocarbon conversion process for producing high-octane gasolines of improved volatility characteristics, and particularly relates to a two-stage process wherein a naphtha is hydroformed in a first stage, and the total hydroformer effluent is passed to a second stage comprising a dealkylation stage wherein the volatility and other characteristics of the reformate are improved.

The current demand for high-octane gasolines is being met by improved hydrocarbon conversion processes. One of the most useful of such processes is the so-called hydroforming process, by which term is meant a reforming process wherein naphtha is contacted with a hydroforming catalyst under elevated pressures and temperatures, and in the presence of hydrogen, whereby the octane-number of the naphtha is substantially increased. During the hydroforming process there is no net consumption of hydrogen, and in fact hydrogen is produced in substantial amounts in the process. The reactions taking place in the hydroforming reaction zone include dehydrogenation reactions particularly of naphthenes, to form aromatic compounds, dehydrocyclization of paraffins to form aromatic compounds, hydrocracking reactions, isomerization reactions, particularly of alkylcycloparaffins and paraffins to their paraffinic isomers.

Hydroforming processes currently used, may be classified in a number of ways, such as fixed, moving or fluidized catalyst bed processes, or alternatively as processes where the catalyst is non-regenerative or regenerative. Generally considered, the catalysts at present used consist of or are compounds of metals of Groups IV, V, VI and VIII of the Periodic Table. Such catalysts, particularly the oxides or sulphides of the metals, are usually deposited on a particulate carrier, e.g. alumina with or without silica. A particularly useful type of catalyst, comprises molybdena, which may be used in either fixed or fluidized bed systems, and is capable of regeneration either continuously or on a cyclic basis. Chromia or cobalt molybdate catalysts are particularly useful in moving bed processes while platinum- or palladium-containing catalysts have hitherto been used mainly in fixed-bed processes, although fluidized processes have been visualized for such catalysts. Platinum or palladium catalysts may be used under non-regenerative conditions, e.g. under pressures of 200—700 psi and temperatures of 850—960° F., or under cyclic regeneration conditions at pressures of 300—500 psi and temperatures of 900—950° F. For fluidized processes, pressures may range from 150—200 psi, and temperatures from 890—940° F.

Naphthas which may be used in such hydroforming processes are preferably virgin naphthas having a boiling range of from 150° to 430° F., e.g. 200° to 350° F., although cracked naphthas, or naphthas obtained from Fischer-Tropsch synthesis may also be used.

While hydroformed naphthas may be produced which satisfy present day requirements on octance number, they usually have volatilities lower than those required to meet current specifications. Thus whilst a volatility of 50% vol. distillate boiling at 230° F. is usually required for fractions boiling in the gasoline boiling range, a hydroformate fraction in the same boiling range will usually only distill 35% vol. at 230° F. The general low volatility characteristics of hydroformates can have undesirable effects when they are blended with constituents having different volatility characteristics. In gasolines, for example, disproportionation of the blend may occur in the inlet manifold during periods of acceleration.

The present invention is concerned with a process for improving the properties of hydroformates, particularly their volatility

characteristics, which involves passing the total effluent without substantial cooling from the hydroformer to a dealkylation zone. The advantages of the present process include an improvement in the volatility characteristics of the hydroformate without loss of yield due to formation of tar. The process of the present invention possesses distinct economic as well as technical advantages, in that according to the invention the total hydroformer effluent, including hydrogen, is passed without cooling to the dealkylation zone. An intermediate heating stage may, however, be required, depending on the temperature of the said dealkylation stage. The formation of tar which normally results from the thermal treatment of hydroformate is probably due to dealkylation processes which take place, for instance on the alkyl-substituted aromatic compounds which are contained in hydroformate, the fractured benzene rings coming together to form tarry constituents. The plentiful supply of hydrogen contained in the hydroformer effluent effectively inhibits this tar formation probably by the active benzene residues preferentially joining with the hydrogen molecules. Other reaction mechanisms may however operate to avoid the formation of tar. The main effect of the thermal cracking in the presence of hydrogen taking place in the dealkylation stage is to lower the boiling point of the aromatic compounds, without any diminution of the octane number.

The second stage of the process of the present invention is a process in which the cracking is limited to dealkylation of the aromatic constituents: This may be effected by passing the reformate vapours plus reformate hydrogen rapidly through a heating coil at a temperature of between 1050° to 1400° F. and a pressure between atmospheric and about 700 psi, the space velocity of the hydroformate expressed as vol. hydroformate per hour/coil volume being between 0.2 and 5, preferably between 0.5 to 2.

The present invention consists of a process for producing a gasoline fraction, comprising hydroforming a naphtha fraction in a hydroforming zone in the presence of a hydroforming catalyst and hydrogen, and passing the total effluent from the hydroforming zone without substantial cooling to a dealkylation zone and therein subjecting it to the action of heat whereby the total normally liquid product recovered from the said dealkylation zone has a greater % by vol. of distillate boiling at 230° F. than that which it is possible to obtain from the hydroformate nomally liquid effluent, and recycling at least a part of the hydrogen from the dealkylation zone to the hydroforming zone.

Having now described the invention, reference may be made to the drawing accompanying the Provisional Specification which diagrammatically illustrates a preferred way of carrying out the invention, wherein a vapourized naphtha, preferably boiling within the range 200° to 400° F. enters through line 1, and together with admitted hydrogen compressed in compressor 2, is heated in furnace 3, whence the naphtha vapours are transferred to the hydroforming zone 4. The temperatures and pressures of the vapours entering the said hydroforming zone will depend upon the type of hydroforming process used. Thus the hydroforming zone may be a multi-unit zone, for example, a fixed multi-bed process using a platinum-containing catalyst, or a single unit fluidized hydroforming zone, using molybdena-containing catalysts. Where platinum catalysts are used, a guard catalyst bed (not shown) may be placed in the feed-line before the hydroforming zone.

The total effluent from the hydroforming zone 4 is transferred via line 5 without substantial cooling to the heating zone 6 whence it enters the dealkylation zone 7, which may be a coil operated under pressures of from 200—700 psi, temperatures of from 1050—1400° F., and a through-put of vol. feed per hour/vol. coil of from 0.5 to 2.0.

The effluent from the dealkylation zone is withdrawn via line 8, cooled in cooling unit 9, and passed via line 10 to the separating zone 11, whence the hydrocarbons are taken via line 12 to the fractionator 13, whence they may be fractionated as required, e.g. into comparatively light and heavy fractions in lines 14 and 15, to recover a gasoline fraction. The gaseous overhead, consisting predominantly of hydrogen is recycled via line 16 to the feed line 1. If desired, make-up hydrogen may be introduced into line 16 via bleed line 17, and the hydrogen-containing stream may be purged as required via purge-line 18.

WHAT WE CLAIM IS:—

1. A process for producing a gasoline fraction comprising hydroforming a naphtha fraction in a hydroforming zone in the presence of a hydroforming catalyst and hydrogen, and passing the total effluent from the hydroforming zone without substantial cooling to a dealkylation zone, and therein subjecting it to the action of heat whereby the total normally liquid product recovered from the said dealkylation zone has a greater percentage by volume of distillate boiling at 230° F. than that which it is possible to obtain from the total normally liquid effluent from the hydroforming zone, and recycling at least a part of the hydrogen from the dealkylation zone to the hydroforming zone.

2. A process as claimed in Claim 1 wherein the dealkylation zone is operated at a pressure of 200 to 700 psi and a temperature of 1050 to 1400° F.

3. A process as claimed in Claims 1 or 2 wherein the said hydroforming zone is a fixed multi-bed hydroforming process employing a platinum catalyst.

4. A process as claimed in Claims 1 or 2 wherein the said hydroforming zone is a fluidized hydroforming zone.

5. A process as claimed in Claim 1 for producing a gasoline fraction substantially as

hereinbefore described and shown in the drawing accompanying the Provisional Specification.

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PROVISIONAL SPECIFICATION

Hydroforming of Naphthas

We, ESSO RESEARCH AND ENGINEERING COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Elizabeth, New Jersey, United States of America, do hereby declare this invention to be described in the following statement:—

The present invention relates to an improved hydrocarbon conversion process for producing high-octane gasolines of improved volatiltiy characteristics, and particularly relates to a two-stage process wherein a naphtha is hydroformed in a first stage, and the total hydroformer effluent is passed to a second stage comprising a thermal treating stage, wherein the volatility and other characteristics of the reformate are improved.

The current demand for high-octane gasolines is being met by improved hydrocarbon conversion processes. One of the most useful of such processes is the so-called hydroforming process, by which term is meant a reforming process wherein naphtha is contacted with a hydroforming catalyst under elevated pressures and temperatures, and in the presence of hydrogen, whereby the octane-number of the naphtha is substantially increased. During the hydroforming process there is no net consumption of hydrogen, and in fact hydrogen is produced in substantial amounts in the process. The reactions taking place in the hydroforming reaction zone include dehydrogenation reactions, particularly of naphthenes, to form aromatic compounds, dehydrocyclization of paraffins to form aromatic compounds, hydrocracking reactions, isomerization reactions, particularly of alkylcycloparaffins and paraffins to their paraffinic isomers.

Hydroforming processes currently used, may be classified in a number of ways, such as fixed, moving or fluidized catalyst bed processes, or alternatively as processes where the catalyst is non-regenerative or regenerative. Generally considered, the catalysts at present used are compounds comprising metals of Groups IV, V, VI and VIII of the Periodic Table. Such catalysts, particularly the oxides or sulphides of the metals, are usually deposited on a particulate carrier, e.g. alumina with or without silica. A particularly useful type of catalyst, comprises molybdena, which may be used in either fixed or fluidized bed systems, and is capable of regeneration either continuously or on a cyclic basis. Chromia or cobalt molybdate catalysts are particularly useful in moving bed processes while platinum- or palladium-containing catalysts have hitherto been used mainly in fixed-bed processes, although fluidized processes have been visualized for such catalysts. Platinum or palladium catalysts may be used under non-regenerative conditions, e.g. under pressures of 200—700 psi and temperatures of 850—960° F., or under cyclic regeneration conditions at pressures of 300—500 psi and temperatures of 900—950° F. For fluidized processes, pressures may range from 150—200 psi, and temperatures from 890—940° F.

Naphthas which may be used in such hydroforming processes are preferably virgin naphthas having a boiling range of from 150° to 430° F., e.g. 200° to 350° F., although cracked naphthas, or naphthas obtained from Fischer-Tropsch synthesis may also be used.

While hydroformed naphthas may be produced which satisfy present day requirements on octane number, they usually have volatilities lower than those required to meet current specifications. Thus whilst a volatility of 50% vol. distillate boiling at 230° F. is usually required for fractions boiling in the gasoline boiling range, a hydroformate fraction in the same boiling range will usually only distill 35% vol. at 230° F. The general low volatility characteristics of hydroformates can have undesirable effects when they are blended with constituents having different volatility characteristics. In gasolines, for example, disproportionation of the blend may occur in the inlet manifold during periods of acceleration.

The present invention is concerned with a process for improving the properties of hydroformates, particularly their volatility characteristics, which involves passing the total effluent from the hydroformer to a thermal treating zone. The advantages of the present process include an improvement in the volatility characteristics of the hydroformate without loss of yield due to formation of tar. The process of the present invention possesses distinct economic as well as technical advantages. Thus the total hydroformer effluent, including hydrogen, is passed without cooling to the thermal treating zone. An intermediate heating stage may, however, be required, depending on the temperature of the said thermal treating stage. The inhibition of tar which normally results from the thermal treatment of hydroformate is probably due to dealkylation process which take place, for instance on the alkyl-substituted aromatic compounds which are contained in hydroformate, the fractured benzene rings coming together to form tarry constituents. The plentiful supply of hydrogen contained in the

hydroformer effluent effectively inhibits this tar formation probably by the active benzene residues preferentially joining with the hydrogen molecules. Other reaction mechanisms may however operate to avoid the formation of tar. The main effect of the de-alkylation reactions taking place in the thermal treating stage is to lower the boiling point of the aromatic compounds, without any diminution of the octane number.

The second stage of the process of the present invention may be a straight thermal cracking process, preferably under conditions whereby the cracking is limited to dealkylation of the aromatic constituents, or the thermal treatment may be a thermal reforming process. Thus the thermal treatment may be a simple treating arrangement, such as passing the reformate vapours plus reformate hydrogen rapidly through a heating coil at a temperature of between 950° F. to 1400° F. Preferred conditions are a temperature between 1000° and 1200° F., a pressure between atmospheric and about 700 psi, the space velocity of the hydroformate expressed as vol. hydroformate per hour/coil volume being between 0.2 and 5, preferably between 0.5 to 2.

In all instances, the pressure in the thermal treating zone should be less than the pressure in the hydroforming zone, to ensure one-way working of the process.

The present invention therefore comprises a process for producing an improved gasoline fraction, comprising contacting a naphtha fraction in a hydroforming zone in the presence of a hydroforming catalyst and hydrogen at elevated temperatures and pressures, and feeding the total effluent from the hydroforming zone to a thermal treating zone operated under conditions whereby there is recovered from the said thermal treating zone a gasoline fraction having at least a distillate volume at 230° F. greater than that which it is possible to obtain from the said hydroformate total effluent, and recycling from the said thermal treating zone at least a part of the hydrogen obtained therefrom, to the said hydroforming zone.

Having now described the invention, reference may be made to the accompanying drawing, which diagrammatically illustrates a preferred way of carrying out the invention.

Referring to the drawing, a vapourized naphtha, preferably boiling within the range 200°—400° F. enters through line 1, and together with admitted hydrogen compressed in compressor 2, and heated in furnace 3, from whence the naphtha vapours are transferred to the hydroforming zone 4. The temperatures and pressures of the vapours entering the said hydroforming zone will depend upon the type of hydroforming process used. Thus the hydroforming zone may be a multi-unit zone, for example, a fixed multi-bed process using a platinum-containing catalyst, or a single unit fluidized hydroforming zone, using molybdena-containing catalysts. Where platinum catalysts are used, a guard catalyst bed (not shown) may be placed in the feed-line before the hydroforming zone.

The total effluent from the hydroforming zone 4 is transferred via line 5 to the heating zone 7, from whence it enters the thermal treating zone 7. This may be a thermal reforming zone, operated under pressures of 250—1000 psi, although the actual operating pressure should be less than that contained in the aforesaid hydroforming zone, and temperatures of from 950° to 1050° F., the residence time within the coils of the thermal reforming zone being from 10—20 secs. Alternatively the thermal treating zone may be operated under hydrodealkylation conditions, e.g. under pressures of from 200—700 psi (the pressure being less than that contained in the hydroformer), temperatures of from 1050—1150° F., and a through-put of vol. feed per hour/vol. coil of from 0.5 to 2.0. If it is desired, high temperature hydrocracking conditions may be employed, for particularly refractory feedstocks, employing cracking temperatures up to 1400° F.

The thermal treating zone may also be a catalytic hydrocracking zone, using preferably a cobalt molybdate catalyst, or a catalyst comprising a mixture of cobalt oxide and molybdena. Such a process may be carried out at temperatures of about 925°—975° F., at pressures of from 220—750 psig, and space velocities of between 0.9—3.6 V/V/Hr.

The effluent from the thermal treating zone is withdrawn via line 8, cooled in cooling unit 9, and passed via line 10 to the separating zone 11, whence hydrocarbon vapours are taken via line 12 to the fractionator 13, whence they may be fractionated as required, e.g. into comparatively light and heavy fractions in lines 14 and 15. The gaseous overhead, consisting predominantly of hydrogen, is recycled via line 16 to the feed line 1. If desired, make-up hydrogen may be introduced into line 16 via bleed line 17, and the hydrogen-containing stream may be purged as required via purge-line 18.

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805,111 PROVISIONAL SPECIFICATION

1 SHEET

This drawing is a reproduction of the Original on a reduced scale.